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BASIC STUDIES ON
DISPERSION HARDENING

QUARTERLY REPORT No. 1,
(11 June) - (11 September, 1963
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L. J. Bonis

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The following is a summary of the progress for the period 11 June - 11 September, 1963 on NASw-726, "Basic Studies on Dispersion Hardening".

INTERFACIAL AND STRAIN ENERGY MEASUREMENTS BETWEEN DISPERSED SECOND PHASE AND MATRIX METAL

Techniques

The measurement of interfacial and strain energies between dispersed second phase and matrix metal is made possible by recent advances in measuring instruments. The interfacial energy is a function of misorientation, therefore the measuring of it will reveal data which makes it possible to calculate the energies present at interfaces.

The methods which will be used are:

- a) X-ray measurements combined with Fourier analysis.
 - b) High powered transmission electron microscopy.
- a) Measurements of lattice strain due to fine dispersed particles and the relation of this strain to the strain energy introduced by these particles.

It is proposed that a straight dispersion hardened system, such as nickel Al_2O_3 , be studied by means of x-ray diffraction to determine the contribution that small coherent or incoherent dispersed particles make to the total strain configuration of

the lattice. It is known that the hardening effect of these particles is due primarily to the strain field introduced by them and is directly related to the strain field and its interaction with dislocations moving through.

Since the particles themselves are relatively hard oxides, such as TiO_2 , SiO_2 , Al_2O_3 , etc., the majority of the interface strain must be accommodated by the surrounding matrix lattice. It is furthermore believed that this strain may possibly be of a magnitude such as to produce measurable line broadening of all x-ray diffraction peaks from the matrix material and that a very careful measurement of this broadening could be directly related to it. It is, of course, necessary to have a strain free specimen to compare with the dispersion hardened materials and to analyze the data in such a fashion as to isolate the strain due to the fine particles. A technique readily applicable to this end is the Fourier analysis developed by Warren and Averbach and fully described by Warren's review article.*

* B. E. Warren, "X-RAY STUDIES OF DEFORMED METALS", Prog. in Metal Physics, Vol. 8, Pergamon Press, 1959, P. 147.

The intensity distribution of an x-ray diffraction peak of the type (001) may be represented as:

$$P_{2\theta} = K(\theta) N_n \sum An(l) \cos 2\pi n h_3 \quad (1)$$

Where: N = Total number of cells

h_3 = Number of reciprocal lattice spacings in direction perpendicular to plane

which is a one dimensional Fourier cosine series whose coefficients $An(l)$ may be written from diffraction theory as:

$$An(l) = \frac{N_n}{N_3} \langle \cos 2\pi l Zn \rangle \quad (2)$$

Where: N_n = Number of cells in a unit length of column perpendicular to diffraction plane

N_3 = Total number of cells in column

These coefficients can be considered as compressed essentially of a size effect and strain effect term and can be separated as follows:

$$\ln A_L(l_0) = \ln A_L^p - 2\pi^2 l_0^2 \langle \Delta L^2 \rangle / n_0^2 \quad (3)$$

where $\left(\frac{\langle \Delta L^2 \rangle}{L^2} \right)^{\frac{1}{2}}$ is equivalent to root mean

square strain.

The terms L refer to the length of a diffracting column = na_0 , $l_0^2 = h^2 + k^2 + l^2$ for any crystalline reflection $h k l$ and a_0 is the lattice constant. For different orders of a set of $(h k l)$ planes a plot of $\ln A_L$ VS l_0^2 for different values of the averaging distance L yields values of the root means square strain and of the particle size coefficient. If one chooses the averaging distance appropriate to the particular case in question - namely one-half the interparticle spacing - one should thus have an unequivocal measure of strain associated with each particle in the dispersion strengthening process.

A very simple test for this procedure would be to take a sample which has no particles dispersed in it and run a very accurate step counted diffraction pattern of five orders (due to the overlapping of third order reflection with other reflections) of $h k l$ for two different $h k l$ planes of the matrix phase. This would be followed by an optimum dispersion in the same matrix for the given composition such as to produce close to optimum hardness, after which the diffraction procedure would be repeated. Using the solution treated sample (of fine grain size to eliminate extraneous effects) as a correction sample, one could then apply the above Fourier analysis to obtain the Al_2O_3 for the appropriate values of L for the particle strengthened material.

The measurements as previously stated would hopefully yield a significant value of $\langle E^2 \rangle^{\frac{1}{2}} = \left(\frac{\langle \Delta L^2 \rangle}{L} \right)^{\frac{1}{2}}$ for the strain as averaged over half of the interparticle spacing within the matrix. This strain would then be directly relatable to strain energy, state of particle coherency, and through an appropriate model, to particle interfacial energy.

The latest x-ray diffraction equipment will be utilized (Picker Biplane Diffractometer). Peaks will be automatically step scanned and a digital print out will record the information which, in turn, shall be fed into a computer and analyzed.

- b) The second method is visual observation of lattice distortion of the matrix around the dispersed particles.

The new Hitachi Model HU-11 electron microscope in our laboratories is one of the latest developments in the field of electron microscopy. The resolution limit of this unit is better than 7 angstrom, which is less than twice that of the theoretical limitations.

With the aid of this instrument we can observe lattice distortion on a thin film of dispersion hardened materials. Method of sample preparation being utilized is electrolytic dissolving (Bollmann technique).

The test will be visual observation, photographic measuring techniques and graded grid measurements of lattice plane distortions by transmission electron microscopy. With the collected data we will be able to draw a map about the strain field around each particle examined.

We will also be able to measure misorientations, (ϕ), which is directly relatable to interfacial energies.

I. Part I - Initial Materials Preparation

A. Materials

As outlined in the basic work statement, the materials to be utilized in the program were nickel-base, dilute solid solution alloys. These were to be internally oxidized to form Ni-Al₂O₃, Ni-TiO₂, and Ni-SiO₂, the fourth alloy, Ni-Th₂O₃, to be obtained commercially.

B. Preparation

It was decided at the outset to fabricate two alloys of each material, one having a low and the other a high volume percent of oxide in order that comparisons of dislocation patterns and movements and x-ray line-broadening could be made within each material system, as well as between different materials.

Some material was available at Ilikon from previous research programs; however, the greater part of the materials had to be fabricated from alloy chips. The fabrication pro-

cedure was as follows: The chips were ball-milled and sieved at periodic intervals to separate out the finer -270 mesh particles. Internal oxidation was carried out using the resultant -270 mesh powder as the matrix in a Lindberg tube furnace. The proper amount of oxygen was provided by a mixture of Ni-NiO (1:8 ratio) powder. All internal oxidation treatments were carried out at 750°C (in low oxygen partial pressures). The powders were then hydrogen reduced to eliminate all traces of NiO which may have been formed on the alloy particles, and furnace cooled under hydrogen (Reference 7).

C. Fabrication

The treated powders were then packed into a rubber hose, and hydrostatically pressed at 30,000 psi. After pressing, the billets were hydrogen reduced in a double reduction process to eliminate nickel oxide which may have formed during packing. The billets were then sintered in the same environment at 900°C for eight hours, after which the sintered billets were canned and extruded at a ratio of 1:40 and 1100°C. The final sample size was about 0.3" diameter in cross-section. A sample of pure nickel powder (-270 mesh) was cold-pressed and sintered under hydrogen, then canned and extruded in a manner analagous to the internally oxidized specimens. The pure nickel sample will be used as a standard for most measurements.

D. Results

The results of the internal oxidation treatments (in terms

of particle sizes and distributions) are shown in Table I for the Ni-Al₂O₃, Ni-TiO₂, and Ni-SiO₂ alloys. The photomicrographs of Figures 1 to 4 show some typical microstructures.

II. Part II - Thinning Techniques and Related Electron Microscopy

A. Preparation for Thinning

The bulk of the initial thinning was carried out on alloy No. IL-4 (with high silica content), since a good deal of this material was available at the beginning for the purpose of establishing thinning procedures. Wafers approximately 1/16" in thickness were sliced from the extruded bars in both transverse and longitudinal sections. The samples were then mounted in de Khotinsky cement for further thinning by grinding and polishing. Mechanical polishing brought section thicknesses to about 0.02 inches and subsequent rolling (interrupted by a short anneal) resulted in final thickness in the area of 0.005 inches. This was found to be an optimum thickness for the start of electrolytic thinning. All work in the program has been carried out on transverse sections of the as-extruded material.

B. Production of Foils by Electropolishing

Techniques for the preparation of thin foils of metals and alloys are described in References 1 and 2. However, thinning of dispersion-strengthened systems is relatively

new, and References 3, 4, and 5 sum up the significant efforts in this area. References 3 and 4 deal with Al-Al₂O₃ (SAP-type) alloys, and Reference 5 with Cu-Al₂O₃, Ni-TiB₂, and Ni-TiC. No specific experience has been encountered in the literature in the area of nickel with dispersed oxides.

At the outset, the thinning technique utilized was the Bollman method (Reference 6). Very briefly, the experimental system employs two stainless steel point cathodes, and two plate cathodes, with the specimen as anode. Initially, the point cathodes are placed about 1 mm from the specimen. In order to avoid preferential polishing at the specimen edges, a "window" is masked off at the specimen center (1-4 cm² in area) and the cathodes are also masked, with the exception of the tips, by means of a nonconducting lacquer.* Electro-polishing is then carried out until a hole just barely appears at the center of the specimen. After this, the point cathodes are withdrawn and subsequent polishing is continued by means of the plate cathodes in order to provide more uniform thinning. In effect, the result is a thin wedge of revolution around the hole, the objective being to obtain a section with a very low wedge angle in order to provide as large an area as possible for viewing by transmission electron microscopy. Figure 5 shows the Bollman fixture with a specimen in place, ready to be set into the polishing electrolyte.

* Microstop, a product of Michigan Chrome and Chemical Company, Detroit, Michigan.

The first attempts at thinning the nickel-silica specimens revealed the following difficulties:

- a. The edges of the specimens showed preferential polishing. This was due to a low current density.
- b. Using a very high current density, preferential polishing occurs at the center of the specimens, but subsequent thinning had to be carried out quite carefully at this point, since the holes can round off, and the thin regions are lost.
- c. At low current densities, an oxide film build-up was observed on the surface of the specimens, and this created much difficulty in obtaining suitable thin films, since many artifacts resulted.

The first group of specimens was prepared using stainless steel cathodes, with the electrolyte composed of:

23% perchloric acid
77% glacial acetic acid

in ice water bath

Voltage: 20-25 volts; Current Density: up to 1 amp/cm²

After polishing, the specimens were washed with methyl alcohol. Usually, the alcohol was insufficient to dissolve the surface residues, and a mixture of the following was used to clean the oxide and other residues from the surfaces:

70% orthophosphoric acid
5% nitric acid
10% glacial acetic acid
15% water

at 95°C

This mixture was used as a straight chemical polish, but, thus far, has not shown good results. Further work will be done with this mixture, however.

Our experience has indicated that an alloy with high volume percent of oxide dispersion gives greater difficulty in thinning than one with a low dispersoid content. This has been acknowledged in References 3, 4, and 5.

Several electropolishing media were used in attempts to determine the best possible system for the thinning of the nickel-silica alloys. The best medium to date has been a bath consisting of:

67% methyl alcohol (abs.)

33% nitric acid (conc.)

Voltage: about 30 volts; Current Density: 0.5 amp/cm²

Figures 6 to 9 indicate some typical results of thinning using the nitric acid-methyl alcohol medium. Figure 6 shows the typical substructure in an area free of dispersoid in alloy IL-4. Figures 7, 8, and 9 show the large silica particles in the IL-4 system, with Figures 8 and 9 showing the selective polishing at the periphery of the particles. Figure 10 shows

the presence of holes in a film where oxide particles have fallen out due to selective attack at the oxide matrix boundary by the electropolish.

Another thinning technique which is being utilized is the jet-machining technique. The experimental layout is shown in Figure 11, and shows the specimen (anode) masked with Microstop, the glass orifice, containing the platinum cathode, an acid reservoir, peristaltic pump system, and power source. The electrolyte consists of a mixture of 10% nitric acid in water containing 25 gm/liter of CrO_3 (after Reference 3). This is an initial thinning method, which should leave some oxide residue. The residue may be eliminated by adding a solvent to the acid, or by a secondary chemical polish using the hot acid mixture noted above.

III. Part III - Work in Progress and in Planning

The current work in progress includes:

- A. The continuation of electropolishing of the other materials, in addition to the nickel-silica alloys, using the nitric acid-methyl alcohol electropolish, and also working with the jet-machining system described above and other electropolishing media.
- B. Identification of particles and residues by electron diffraction.

- C. Determination of dislocation structures and pinning by dispersoid particles by transmission electron microscopy.
- D. Heat treatments of alloys for agglomeration studies.
- E. Initial efforts in line-broadening studies by x-ray diffraction.

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5. Murphy, R. J., V. Sadagopan, and N. J. Grant, "Investigation of the Strengthening Mechanisms of Dispersion-Strengthened Alloys", ASD-TDR-62-734, November, 1962.
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TABLE I

COMPOSITION AND STRUCTURAL DATA ON INTERNALLY OXIDIZED NICKEL ALLOYS

| Alloy No. | Solute Wt. % | Volume % oxide* | Int. Oxidation time, hours | Particle Size | | Interparticle Spacing | |
|-----------|--------------|-------------------------------------|----------------------------|---------------|------|-----------------------|------|
| | | | | Range** | Av. | Range*** | Av. |
| IL-1 | 1.25 Al | 5.58 Al ₂ O ₃ | 51 | 100-500 | 200 | 0.1-0.5 | 0.25 |
| IL-2 | 2.27 Al | 10.44 | 60 | 100-1800 | 500 | 0.5-1.5 | 0.75 |
| IL-3 | 1.17 Si | 10.5 SiO ₂ | 48 | 200-5000 | 1000 | 0.5-2 | 0.9 |
| IL-4 | 2.25 Si | 21.0 | 57 | 1000-10,000 | 3500 | 1-5 | 2.5 |
| IL-5 | 2.05 Ti | 6.4 TiO ₂ | 67 | 150-2000 | 650 | 0.5 | 0.5 |
| IL-6 | 3.08 Ti | 7.8 | 81 | 1000-10,000 | 3500 | 1-5 | 2.5 |

* Internally oxidized at 750°C

** By electron microscope

*** Between oxide clusters

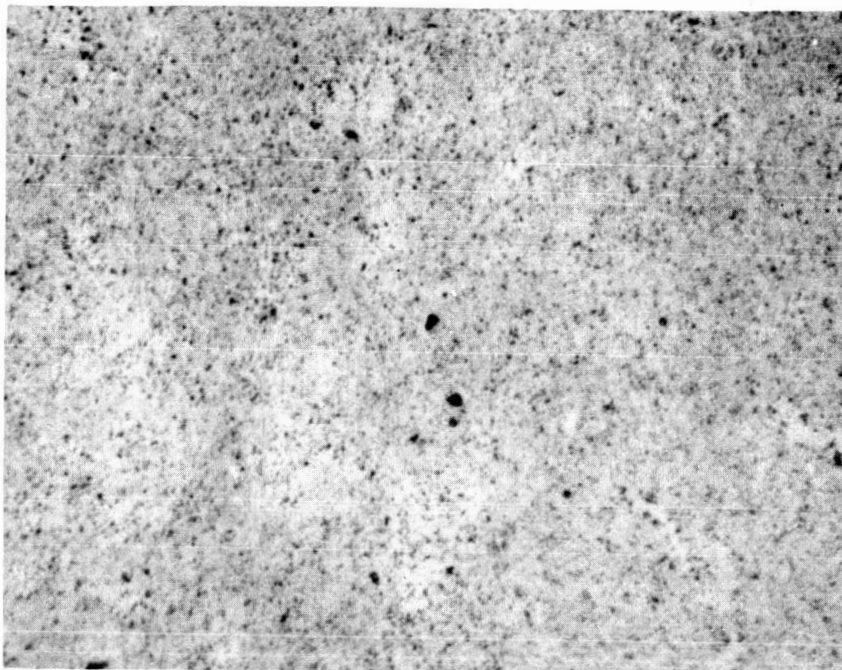


Fig. 1 Typical Microstructure Showing
Low Volume % Oxide Ni-Al₂O₃ 1000X

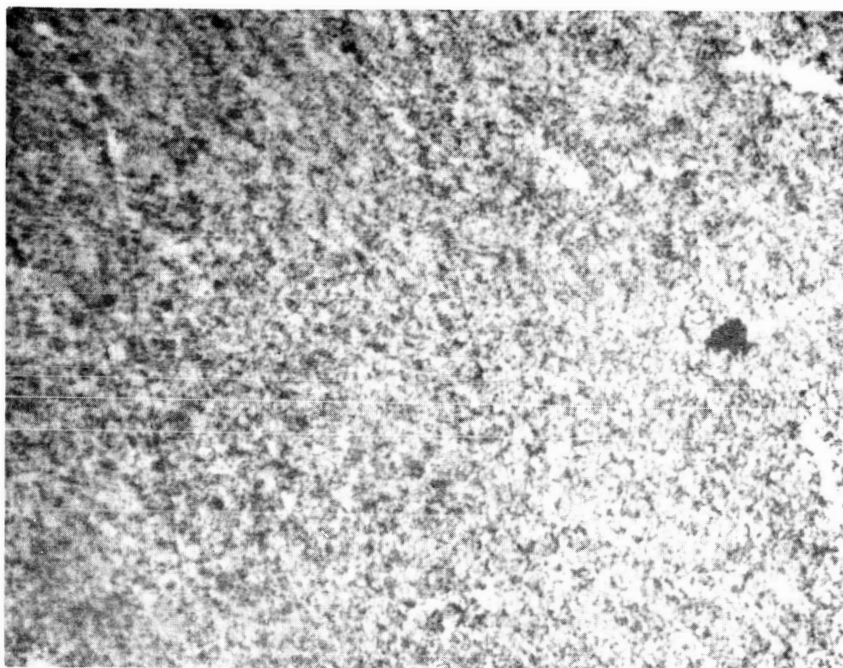


Fig. 2 Typical Microstructure Showing
High Volume % Oxide Ni-Al₂O₃ 1000X

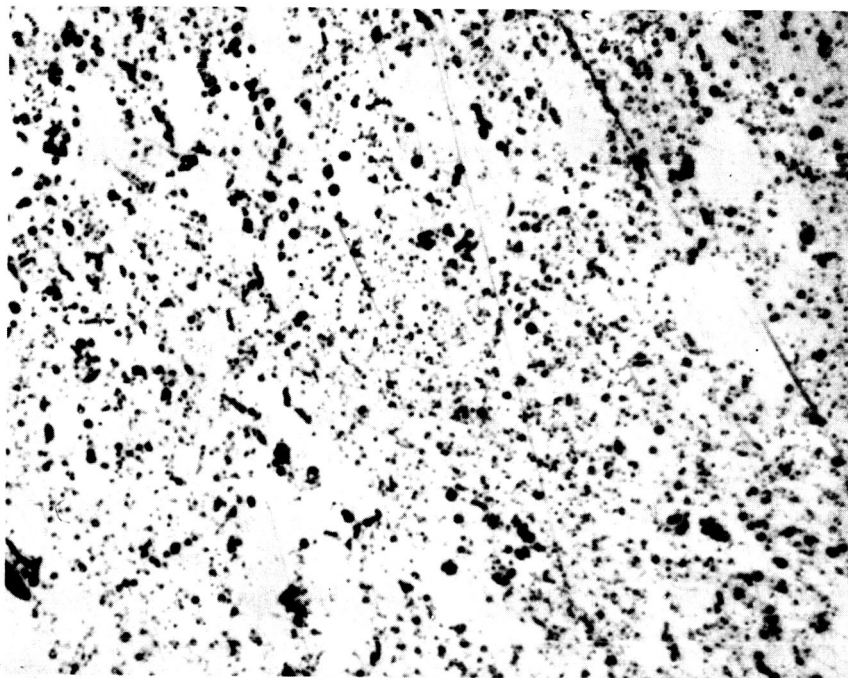


Fig. 3 Typical Microstructure Showing
Low Volume % Oxide Ni-SiO₂ 1000X

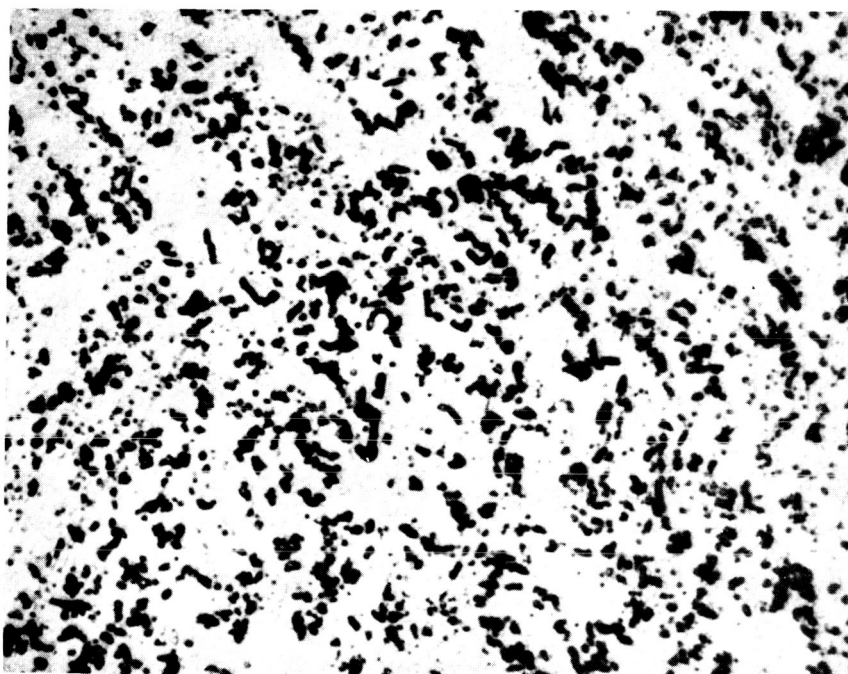


Fig. 4 Typical Microstructure Showing
High Volume % Oxide Ni-SiO₂ 1000X

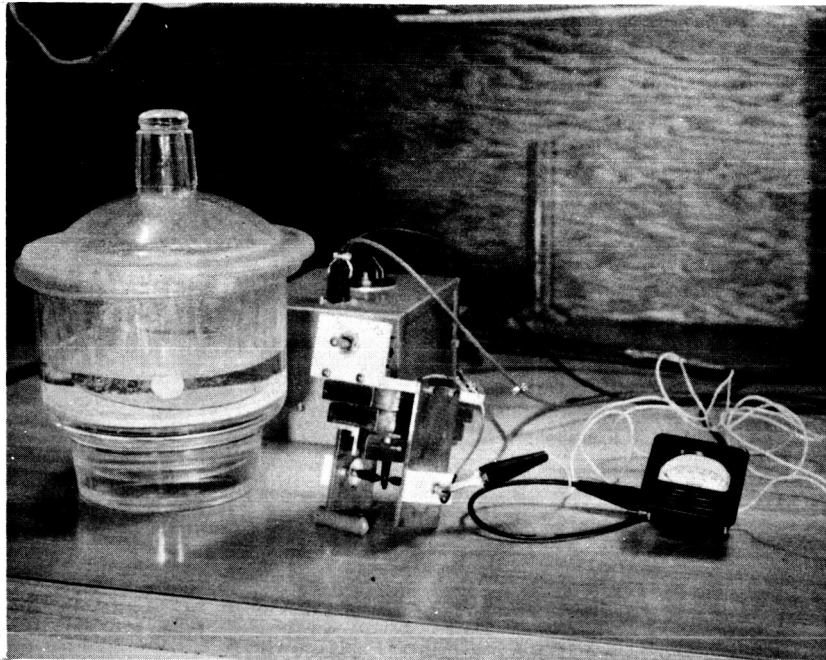


Fig. 5 Bollman Fixture with a Specimen
in Place, ready to be set into
the Polishing Electrolyte

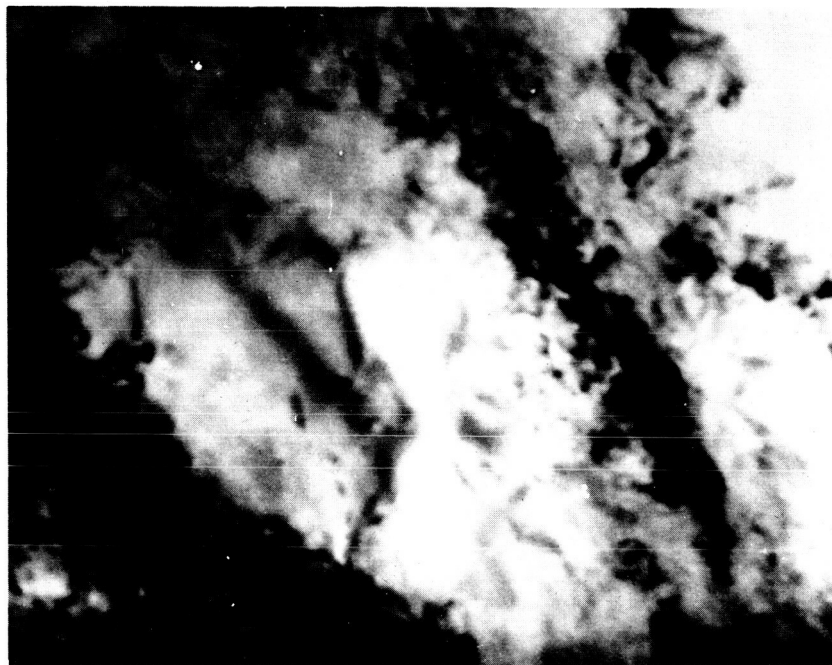


Fig. 6 Typical Microstructure in an Area
Free of Dispersoid in Alloy IL-4 220,000X



Fig. 7 Microstructure of IL-4 Showing Large Silica Particles 52,000X



Fig. 8 Microstructure of IL-4 Showing Large Silica Particles 86,000X



Fig. 9 Typical Microstructure of IL-4
60,000X

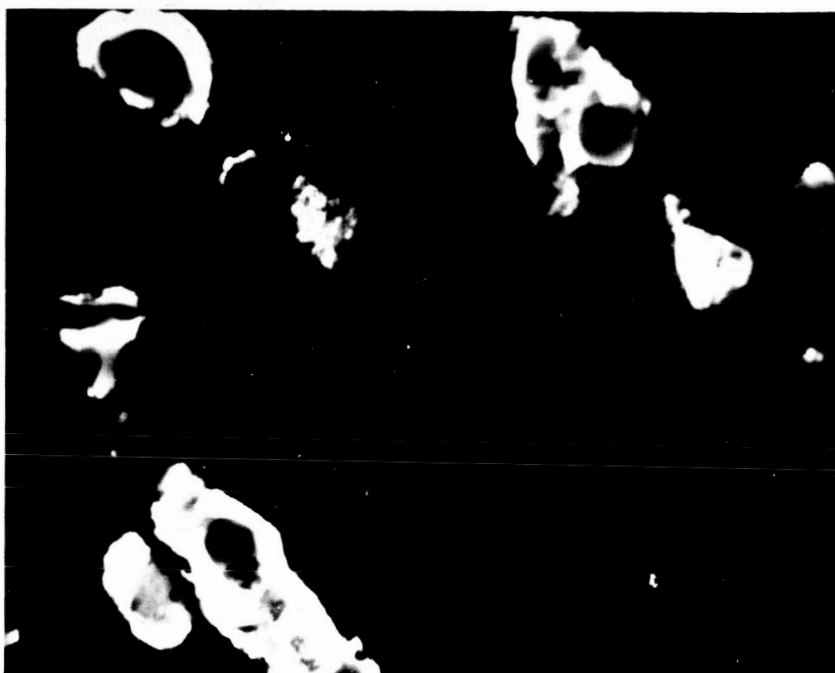


Fig. 10 Selective Polishing at the Periphery
of the Particles. The Presence of
holes in a film where Oxide Particles
have fallen out.
16,000X

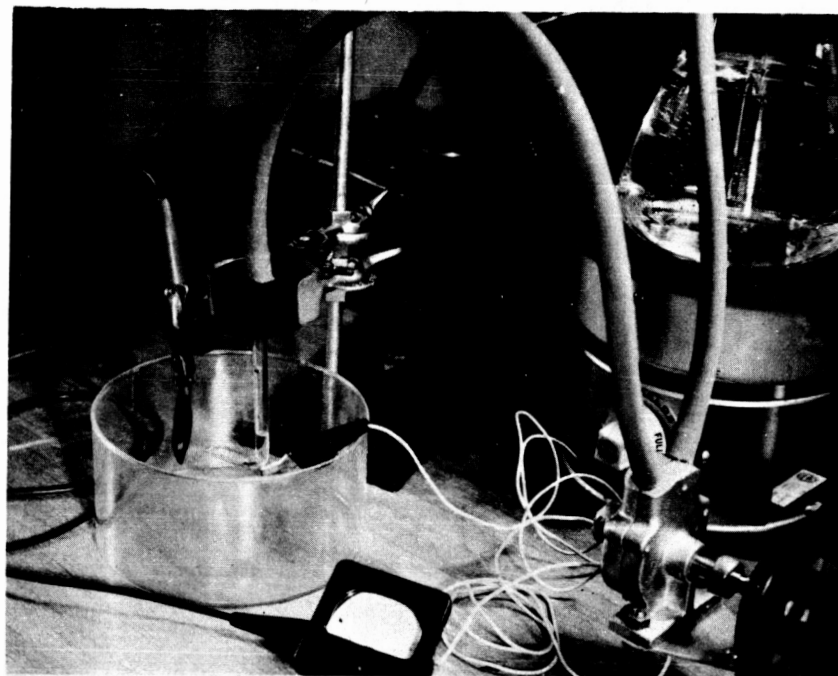


Fig. 11 Experimental Layout for Jet-Machining Technique